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22 Oct 2001

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2001-203**
Ralf Haiges (USC) and Karl Christe (ERC), "A New Synthesis of Anhydrous Cesium Salts"

Inorganic Chemistry (Journal)
(Deadline: N/A)

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A New Synthesis of Anhydrous Cesium Salts

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University of Southern California, Loker Hydrocarbon Research Institute, University Park, Los Angeles, California, 90089, and Air Force Research Laboratory, Edwards AFB, California, 93524

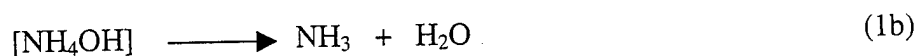
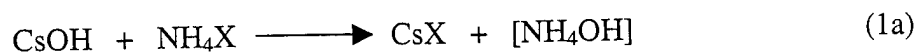
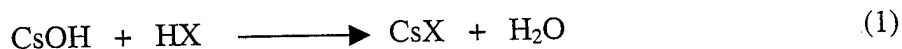
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Introduction

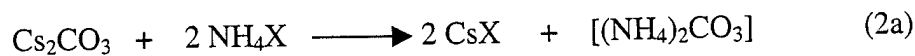
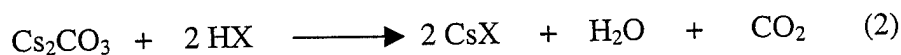
Contrary to ammonium salts many cesium salts are extremely hygroscopic. Consequently, anhydrous ammonium salts are readily available in anhydrous form by neutralizing the corresponding acids with ammonia, but their conversion to anhydrous cesium salts is difficult.¹

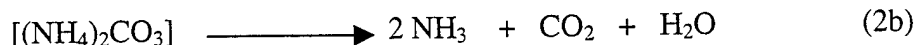
General methods for the preparation of cesium salts include:

- (i) The neutralization of CsOH with the corresponding acid (1) or its ammonium salt (1a,b)²:



- (ii) The reaction^{3,4} of cesium carbonate with the corresponding acid (2) or its ammonium salt (2a,b)²:

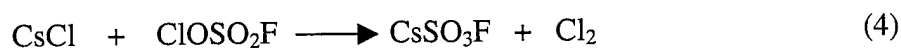




(iii) The reaction⁵ of CsCl with a stronger acid (3):



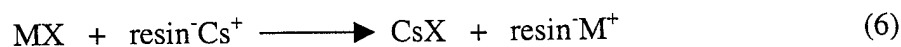
(iv) The reaction⁴ of CsCl with a positive halogen containing compound (4):



(v) Metathetical reactions^{6,7} (5):



(vi) Ion exchange reactions⁸ using cation exchange resins (6):

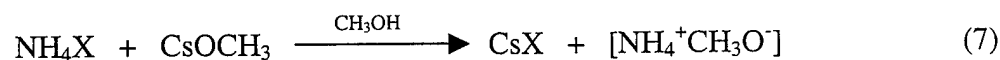


These reactions suffer from the following drawbacks. In reactions (1), (2), and frequently also in (6) water is formed either as a by-product or used as a reaction medium and often cannot be removed subsequently without destroying the desired cesium salt. The displacement reaction (3) works only for acids such as TeF_5OH ⁵ that are significantly stronger than HCl, and the metathetical reaction (5) requires the two starting materials and one of the products to be highly soluble and the second product to be very insoluble in a volatile solvent. In addition, product purity can present a major problem in the metathetical reactions and require recrystallizations. Reaction (4) is relatively complicated and not a convenient general method. It was therefore desirable to find a convenient method for converting ammonium salts into pure anhydrous cesium salts in high yield.

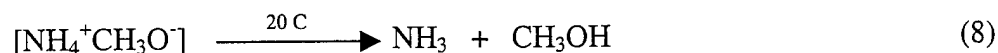
Results and Discussion

A convenient method for the preparation of anhydrous cesium salts was discovered (7). It is based on the thermal instability of ammonium methoxide (8) that drives the reaction to

completion. This thermally unstable by-product product can easily be pumped off at room temperature as NH_3 and CH_3OH .



($\text{X} = \text{Cl}, \text{CH}_3\text{CO}_2, \text{N}(\text{NO}_2)_2, \text{ClO}_4$)



The principle of our approach was demonstrated for the reactions of cesium methoxide with ammonium dinitramide, ammonium perchlorate, ammonium chloride and ammonium acetate in methanol and afforded the corresponding cesium salts in high yield and purity. Although the reaction was demonstrated only for these 4 salts, it should be generally applicable to any other ammonium salt that is soluble in CH_3OH and compatible with CH_3OH and NH_3 . Because of their strong oxidative nature, the reactions with ammonium dinitramide and ammonium perchlorate were carried out at -40°C and -50°C , respectively, to avoid attack of the solvent by the anions, but in the case of less reactive ions it can be carried out at room temperature. The only by-products are methanol and ammonia and, if exact amounts of starting materials are used, the yield of the desired cesium salt is quantitative and its purity is excellent. Even if reaction (7) should constitute only an equilibrium, such an equilibrium is continuously shifted to the right and reaction (7) is driven to completion by the continuing removal of one of the products, i. e., $\text{NH}_4^+\text{CH}_3\text{O}^-$.

If one of the starting materials is used in excess or contains some common and hard to avoid impurities, such as NO_3^- in $\text{N}(\text{NO}_2)_2$,^{1,8} it is advisable to purify the crude product by recrystallization from methanol and washing of the recrystallized product with cold methanol

(-20 °C). The purity and anhydrous nature of our products was established by infrared and Raman spectroscopy and was shown to be excellent.

The above results demonstrate the potential of cesium methoxide as a very useful general reagent for the conversion of ammonium salts into anhydrous cesium salts. This can be of particular interest when the corresponding ammonium salts are readily available on a large scale, as is the case for the energetic propellant ingredients $\text{NH}_4^+\text{ClO}_4^-$ and $\text{NH}_4^+\text{N}(\text{NO}_2)_2^-$.

Experimental Section

Materials and Apparatus. All reactions were carried out in Pyrex glass vessels that were closed by Teflon-FEP valves. Volatile materials were handled on a Pyrex glass vacuum line. Nonvolatile solids were handled in the dry argon atmosphere of a glove box. The heptane was dried over potassium, the methanol was dried over molecular sieve and both were distilled prior to their use on a grease-free Pyrex glass vacuum line.

Synthesis of CsOCH_3 . In the dry box, cesium (1.32 g, 10.00 mmol) was placed into a Pyrex glass vessel equipped with a Teflon-FEP valve. The vessel was then connected to the Pyrex glass line, and 10 mL of dry heptane and 0.5 mL of dry methanol were condensed in at -196 °C. The reaction mixture was allowed to warm to 20 °C. On melting of the solvent, strong gas evolution was observed. After completion of the gas evolution, the volatile products (H_2) were pumped off at -196 °C and an additional amount of 0.5 mL of dry methanol was condensed in. This procedure was repeated until no unreacted cesium remained in the mixture. After removal of all volatile compounds at 25 °C white solid CsOCH_3 (1.49 g, 10.00 mmol) was obtained in quantitative yield.

General Procedure for the Synthesis of Anhydrous Cesium Salts. A solution of CsOCH_3 (164 mg, 1.00 mmol) in 5 mL of dry methanol is added at the desired temperature to a solution of 1.00 mmol of the corresponding ammonium salt in 5 mL of dry methanol. In the cases of the perchlorate, chloride and dinitramide, white precipitates are immediately formed that can either be isolated by filtration after concentrating the solution or the complete reaction mixture can be pumped to dryness at 25 °C. Any potential impurities can be removed either by recrystallization or washing of the precipitate with a small amount of cold methanol. The nonvolatile white solid residue consists of the corresponding cesium salt in essentially quantitative yield. The absence of the ammonium ion in the product is verified by infrared and Raman spectroscopy.

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- (2) Schumacher, J. C. in Kirk-Othmer, "Encyclopedia of Chemical Technology," second edition, Vol. 5, pge 69, Interscience Publishers, John Wiley & Sons, Inc. New York (1964).
- (3) See for example the preparation of CsNO₃: Christe, K. O.; Wilson, W. W.; Wilson, R. D. *Inorg. Chem.* **1980**, *19*, 1494.
- (4) See for example the preparations of CsPO₂F₂, Cs₂SO₄, and CsSO₃F: Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Chem.* **1980**, *19*, 3046.
- (5) See for example the preparation of CsOTeF₅: Mayer, E.; Sladky, F. *Inorg. Chem.* **1975**, *14*, 589.
- (6) See for example the preparation of CsIO₄: Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Chem.* **1981**, *20*, 2104.
- (7) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; 2nd ed.; Butterworth, Heinemann: Oxford, 1998; p 867.
- (8) Bottaro, J. C.; Penwell, P. E.; Schmitt, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 9405; although the example given in this paper involves the exchange of Cs⁺ for other cations, the direction of the ion exchange can be reversed.

SYNOPSIS

Ralf Haiges and Karl O. Christe*

Inorg. Chem. **2001**, ...

A New Synthesis of Anhydrous Cesium Salts

A new method is described for the conversion of ammonium salts into anhydrous cesium salts in high purity and yield. It is based on a metathetical reaction of $\text{Cs}^+\text{OCH}_3^-$ with the corresponding ammonium salt in methanol solution and offers the advantage of the undesired by-product, $\text{NH}_4^+\text{OCH}_3^-$, dissociating at room temperature into volatile NH_3 and CH_3OH that can readily be pumped off. The method was successfully demonstrated for the syntheses of $\text{CsN}(\text{NO}_2)_2$, CsClO_4 , CsCl , and CsCH_3CO_2 .

